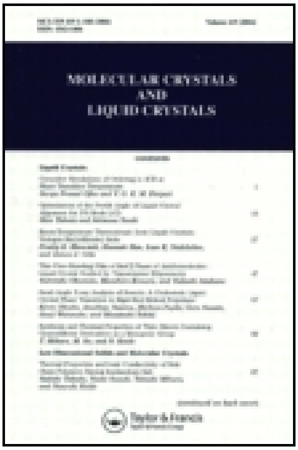

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Possibility of Solitions with Charge ± e/2 in Highily Correlated 1:2 Salts of Tetracyanoqutnodimethane (TCNQ)

M. J. Rice [a] & E. J. Mele [a]
[a] Xerox Webster Research Center, Xerox Square-114, rochester, N.Y., 14644
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POSSIBILITY OF SOLITONS WITH CHARGE ± e/2 IN HIGHLY CORRELATED 1:2 SALTS OF TETRACYANOQUINODIMETHANE (TCNQ)

M.J. RICE and E.J. MELE
Xerox Webster Research Center
Xerox Square-114, Rochester, N.Y., 14644

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Solitons with fractional charge ± e/2 might be experimentally realized in the highly correlated 1:2 salts of TCNQ if the quarter filled TCNQ chains of these compounds correspond to linear Hubbard chains dominated by the on-site Coulomb repulsion. The low-temperature current carrying excitations of the TCNQ chains would consist of thermally activated pairs of such fractionally charged solitons. The addition of a single electron to a TCNQ chain would lead to the formation of two identical solitons with half-integer charge.

In a recent paper Jackiw and Schrieffer[1] have drawn a fascinating parallel between the spinless charged soliton states which arise in a half-filled Peierls insulator[2-7] and those which arise in a one-dimensional model of relativistic fermions due to Jackiw and Rebbi[8] (JR). In the Peierls system the electrons are coupled to the dimerization field of the linear chain while in the JR model Dirac fermions are coupled to a broken symmetry Bose field which plays the role of a spatially dependent fermion rest mass. Common to the two systems is the remarkable effect of a solitonic phase-reversal in the respective Bose field to produce a localized mid-gap fermion state ψ_o which is screened by a local deficiency in occupied continuum fermion states equal to one-half of a state per spin. For the Peierls system the fractional nature of the latter screening is masked by the spin degeneracy of the electron. Two degenerate spinless soliton states arise with charge $Q = \pm \lambda(e/2)$ depending on whether ψ_o is completely filled or empty. Here $\lambda = 2$ denotes the spin degeneracy of the electron and e the charge on an electron. For the JR system, however, the one-dimensional Dirac fermions are spinless and, consequently, two degenerate zero-energy fermion states with fractional charge $Q = \pm e/2$ are associated with the soliton, depending on whether ψ_o is occupied or empty. Here e denotes the charge on the fermion.

The spinless soliton states with charge $Q = \pm e$ which arise for the half-filled Peierls insulator have an experimental realization[5,6] in the linear chain polymer trans-polyacetylene.[9] In this paper we suggest that the spinless soliton states with charge $Q = \pm e/2$ characteristic of the JR system might be experimentally realized in the highly correlated 1:2 charge-transfer salts of tetracyanoquinodimethane (TCNQ).[10] There exists strong experimental evidence[10] to support the view that the one-quarter-filled linear TCNQ chains of these salts are linear Hubbard chains[11] close to the strong coupling limit $U/4t_o \to \infty$, where U denotes the on-site Coulomb repulsion and $4t_o$ the band width of the one-electron tight-binding Bloch states in the absence of U. In the latter limit there is a complete decoupling of the electronic translational and spin degrees of freedom[12] and it has been rigorously shown[13] that in this limit the linear Hubbard chain with $\nu = 1/2$ or $\nu = 3/2$ electrons per atom dimerizes to become a half-filled Peierls insulator with one-half of a spinless fermion per atom. In other words a spinless analog of the usual half-filled Peierls system is arrived at and for which, therefore, the existence of solitons with half-integer charge may immediately be anticipated.

We show that the highly correlated dimerized Hubbard chain posseses the following soliton-related properties:

(a) the addition of a single electron or hole to the chain leads to the formation of two spinless soliton states with charge $Q = e/2$ for the case of the electron and charge $Q = -e/2$ for the case of the hole.

(b) in the limit of weak electron-lattice coupling the energy of formation of a fractionally charged soliton is Δ/π, where 2Δ denotes the energy gap of the spinless Peierls system.

(c) the dominant low-temperature current carrying excitations of the chain will consist of thermally activated pairs of fractionally charged solitons of the form (e/2, -e/2).

(d) light with frequency $\omega \gtrsim 2\Delta/\hbar$ or $\omega \gtrsim U/\hbar$, will lead to the photogeneration of the soliton quartets (e/2, e/2, -e/2, -e/2).

Before commencing our analysis we note that a result similar to the result (a) quoted above has previously been obtained by Hubbard[14] for a highly correlated chain ($U >> 4t_o$) in which the electronic coupling to the lattice is neglected but a large nearest neighbour Coulomb repulsion V between electrons is included. In the limit $(V/2t_o) \to \infty$, the ground state of the quarter-filled chain is a Wigner lattice in which every other site of the chain is occupied by an electron. There is a two-fold degeneracy of the ground state corresponding to the two possible orderings of the charge alternation along the chain. Treating the hopping term in the Hamiltonian as a small perturbation Hubbard argued that an extra electron would enter the quarter-filled chain as two propagating defects in the Wigner lattice, each carrying one-half of the charge of the added electron. In this limit ($V >> 2t_o$) each defect consists of a pair of adjacent occupied sites (or "dimers") which locally reverses the order of the charge alternation of the Wigner lattice. These defects, therefore, have the character of soliton excitations. They have been discussed in a subsequent rigorous development of Hubbard's work by Fowler and Puga.[15] In the latter work, however, the question and nature of the fractional charge carried by the excitations is not explicitly investigated. The feature which Hubbard's system has in common with the present system is the condensation of a gas of spinless fermions into a charge-density-wave (CDW) possessing a two-fold commensurability with the underlying lattice. The occurrence of solitons with charge $Q = \pm e/2$ for both systems is thus understandable from a common standpoint. The essential physical difference between the two systems, however, is that, in the former, the CDW ground state is stabilized by the nearest neighbour Coulomb repulsion V, while in the latter, the CDW ground state is stabilized by the lattice dimerization. That extra electrons added to a highly correlated Wigner lattice at the quarter-filled band level would render the Wigner lattice conducting was noted a few years ago by Lee, Rice and Klemm.[16] An earlier phenomenological analysis by Rice, Bishop, Krumhansl and Trullinger[17] had implied that an M-fold commensurate CDW condensate would become conducting via the thermal excitation of phase solitons ("ϕ - particles") with charge $Q = \pm \lambda e/M$.

In the limit of infinite on-site Coulomb repulsion U the behavior of the linear Hubbard chain with ν electrons per atom is equivalent to that of a composite system of N_s independent spinless fermions and N_σ independent spins where[13]

$$N_s = |(1-\nu)|\,N \qquad 0 \leq \nu \leq 2 \tag{1}$$

$$N_\sigma = \nu N \qquad 0 \leq \nu \leq 1 \tag{2a}$$

$$= (2-\nu)\,N \qquad 1 < \nu \leq 2 \tag{2b}$$

and N ($\to \infty$) is the number of atoms in the chain. The Hamiltonian describing the system is

$$H = H_L - \sum_{n=1}^{N} (t_{n+1,n} c^+_{n+1} c_n + \text{h.c.}) - h\mu_B \sum_{\ell=1}^{N_\sigma} \sigma^z_\ell \tag{3}$$

where c^+_n and c_n denote creation and destruction operators for a spinless fermion at the atomic site n and $t_{n+1,n}$ is a hopping integral for the transfer of a spinless fermion from the (n+1)th to the nth site and is identical to the matrix element for the transfer of an electron from the (n+1) th to the nth site in the original Hubbard Hamiltonian. H_L denotes the lattice energy of the linear chain, h a constant external magnetic field and σ^z_ℓ the z-component of the Pauli matrix for the ℓ th independent spin. The decomposition (1)-(2b) and its description by the Hamiltonian (3) is valid for an arbitrary set of nearest-neighbour hopping integrals, $\{t_{n+1,n}\}$,[13] i.e., for a linear chain of arbitrary spaced atoms. Consequently, the usual Peierls argument may be rigorously applied to the system of spinless fermions.

For small displacements u_n of the nth atomic site from its position in a uniformly spaced linear chain we may introduce

$$H_L = (1/2M) \sum_{n=1}^{N} \dot{u}_n^2 + (1/2)K \sum_{n=1}^{N} (u_{n+1} - u_n)^2 \tag{4}$$

and

$$t_{n+1,n} = t_o - \alpha(u_{n+1} - u_n) \tag{5}$$

where, in (4), M denotes the atomic mass and K a harmonic spring constant, and, in (5), t_o is the hopping integral characteristic of a uniformly spaced chain and α denotes the derivative of $t_{n+1,n}$ with respect to the inter-site separation.

For $\nu = 1/2$ or $\nu = 3/2$ there is one-half of a spinless fermion per atom; consequently the linear chain undergoes a Peierls dimerization with a ground state displacement field

$$u_n = (-1)^n \varphi \tag{6}$$

where $\phi = \pm u_o$ and u_o is a constant. The Peierls gap, 2Δ, introduced in the energy spectrum of the spinless fermions, is given by $\Delta = 4\alpha u_o$. For weak spinless fermion-lattice coupling, $\lambda_s = 2\alpha^2/\pi t_o K << 1$, $\Delta = (8t_o/2.72)\exp(-1/\lambda_s)$.

The soliton related properties (a) - (d) may now be arrived at. We first note that a soliton distortion in the dimerization amplitude ϕ, interpolating between the two ground-state amplitudes $\pm u_o$, removes one-half of a state from the filled spinless fermion valence band (lower Peierls sub-band). Since the minimum number of spinless fermions that can be removed from the latter band is unity, it follows that soliton distortions may be created only in the form of soliton-anti-soliton pairs.

The single spinless fermion which is removed from the valence band by the presence of such a pair may fill the localized mid-gap state ψ_o of either soliton. Therefore, depending on whether ψ_o is occupied or not the charge on either soliton is $Q = \pm e_s/2$ where e_s is the charge associated with a spinless fermion. The latter charge is $e_s = e$ for $\nu > 1$ and $e_s = -e$ for $\nu > 1$. Consequently, the fractional soliton charges are

$$Q = (e/2)\,\mathrm{sgn}\,(\nu-1) \qquad (\psi_0 \text{ occupied}) \qquad (7a)$$

$$= (-e/2)\,\mathrm{sgn}\,(\nu-1) \qquad (\psi_0 \text{ unoccupied}). \qquad (7b)$$

The formation of these charged states is schematically illustrated in Fig. 1.

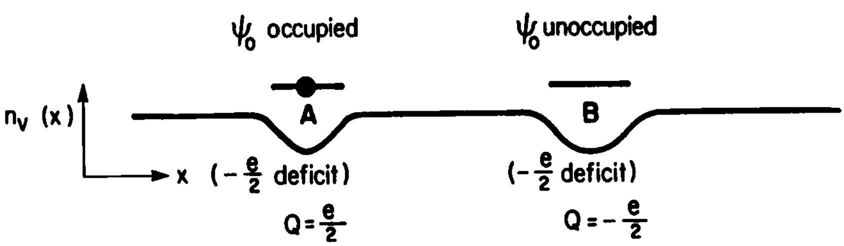

FIGURE 1. Schematic illustration of formation of half-integer charged soliton states. A soliton and antisoliton distortion present in the dimerization amplitude at A and B, respectively, induce localized mid-gap states ψ_o which are screened by a charge deficit of -e/2 in the local valence band charge density $n_v(x)$. If the single spinless fermion removed from the latter is placed in ψ_o at A, leaving ψ_o at B empty, the net charge on the soliton at A is $Q = e/2$ while that on the antisoliton at B is $Q = -e/2$.

The energy of formation, $2E_s$, of a pair of (widely separated) solitons may be immediately arrived at from the work of Takayama et al.,[7] (TLM theory). The only modification required in the present employment of this theory, valid for the weak coupling limit $\lambda_s >> 1$, is the omission of spin-degeneracy in summing over occupied valence band states. We thus obtain

$$E_S = \Delta/\pi \tag{8}$$

i.e., formally one-half of the TLM result. (Note, however, that $\Delta = \Delta' \exp(-1/2\lambda_s)$, where $2\Delta'$ is the Peierls gap with spin degeneracy.)[8] The functional form of the soliton is $\phi(x) = \pm u_o \tanh(x/\zeta)$, with half-width $\zeta = (2t_o/\Delta)a$, where a is the lattice constant of the undimerized Hubbard chain.

We now consider the addition of a single electron to the dimerized Hubbard chain. It is seen from (1) and (2) that the addition of a single electron to the chain decreases the number of spinless fermions by one and increases the number of independent spins by one for $\nu < 1$ and vice-versa for $\nu > 1$. For $\nu < 1$ the spinless fermion may be removed by the creation of a pair of solitons each with ψ_o empty. According to (7b) the charge on each soliton is $e/2$. The cost in energy is $2\Delta/\pi$. For $\nu > 1$, the additional spinless fermion may be added to the system by the creation of a pair of solitons each with ψ_o filled, again with an energy cost of $2\Delta/\pi$. By (7a) the charge on either soliton is $e/2$. Since $2\Delta/\pi$ is an energy less than that, Δ, required to add or to remove a spinless fermion to or from the available continuum states in the absence of soliton distortions, it follows that an extra electron added to the dimerized Hubbard chain will lead to the formation of two spinless soliton states with charge $e/2$. A similar argument shows that a hole added to the system leads to the formation of two similar states with charge $-e/2$.[18]

The result (8) has an interesting implication for the nature of the low-temperature ($k_BT << \Delta$) current-carrying excitations of the linear chain in the absence of added charge. The energy which would be required to promote a spinless fermion from the top of the filled valence band to the bottom of the empty conduction band (upper Peierls sub-band) is 2Δ. By contrast, the energy required to create a soliton pair would be $2\Delta/\pi$, or approximately three times smaller.[19] Thus, the dominant low-temperature current carrying excitations of the chain will consist of thermally activated pairs of positively-and negatively-charged soliton states, (e/2, -e/2).

At low-temperatures quartets of fractionally charged solitons may be indirectly excited by light with frequency $\omega \gtrsim 2\Delta/\hbar$, i.e., by the relaxation of photo-excited spinless fermion-hole pairs, (e,-e) $\rightarrow$ (e/2, e/2, -e/2, -e/2). We also note that light with frequency $\hbar\omega \gtrsim U$ will lead to the excitation of a doubly occupied electronic site in the Hubbard chain, i.e., to a situation in which the number of doubly occupied sites and the number of unoccupied sites are each increased by one. A spinless fermion-hole pair, which may relax to a soliton quartet, is therefore photoexcited with the destruction of two independent spins.

In the organic charge-transfer salts of TCNQ the electrons delocalized along the TCNQ chains are coupled not only to the instantaneous positions of the TCNQ molecule but also to the instantaneous positions of the atomic constituents of the TCNQ molecule. Consequently a Peierls distortion will invariably involve intramolecular distortion as well as intermolecular distortion. It is believed that the Peierls state is dominantly stabilized by intramolecular distortion in typical situations, although its observation by diffuse X-ray scattering is inhibited by the smallness of the intramolecular displacements involved.[20] The present theoretical discussion based on the Hamilton (3) may be repeated for the case of an intramolecular Peierls dimerization, with similar results for soliton properties.[21]

Of the several highly correlated 1:2 TCNQ salts[22] studied to date dimethylferrocenium (DMFC) $TCNQ)_2$ and the ingeniously prepared organic "alloy"[23] (N-methyphenazinium)$_{0.5}$ (Phenazine)$_{0.5}$ $(TCNQ)_2$ or $(NMP)_x(Phen)_{1-x}$ $(TCNQ)_2$ would be of particular interest from the standpoint of the observation of possible soliton properties. In (DMFC) $(TCNQ)_2$ equally spaced TCNQ molecules in the quarter-filled (TCNQ) stacks exhibit an intramolecular dimerization.[22] For the quarter-filled phenazine compound recent X-ray diffuse scattering studies have revealed the presence of a weak dimerization along the TCNQ stacks which, interestingly, is found to persist for small deviations of phenazine concentration from 0.5 in the (NMP) (Phen) donor chain.[24] An incommensurate Peierls distortion at "$4k_F$" would be identifiable in this experiment from Bragg scattering at q = (π/a) (1 + 2C). On the other hand, accommodation of the 2C "excess"$^{\pi}$ carriers in a random soliton lattice would result in the pinning of the diffuse scattering at π /a for small C with a width which increases as 2 π C/a. This decreased correlation length due to randomly situated solitons apparently explains the observed[24] anomalously broad diffraction profile centered at q = π/a. Within the context of the theoretical discussion of this paper, the system $(NMP)_{0.5-C}$ $(Phen)_{0.5+C}$ (TCNQ), with C < < 1, would constitute a "spinless" analog of lightly-doped polyacetylene.

In summary we note that the highly correlated one-dimensional organic charge transfer salts prepared at or near the quarter-filled band level may exhibit solitons with half-integer charge. These defects would be a solid state manifestation of the fractionally charged states discovered by Jackiw and Rebbi in a one-dimensional relativistic field theory. Finally, the pinning of X-ray diffuse scattering spectra at π /a in the organic 'alloy' $(NMP)_{0.5+C}$ $(Phen)_{0.5-C}$ (TCNQ) for C < 10%[24] appears attributable to the expected formation of such fractionally charged defects.

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This paper is dedicated to the memory of John Hubbard.

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